



Emission reduction by means of low temperature plasma

PSO project no. FU3401

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Risø-I-2380(EN)

Emission reduction by means
of low temperature plasma
PSO project no. FU3401

Final report

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Title:

Emission reduction by means of low temperature plasma

Department:

Optics and Plasma Research

Abstract (max. 2000 char.):

The work performed during the project is summarised. In the project we focused on removal of nitrogen oxides NO_x (NO, NO₂) and, in particular, on removal of nitrogen monoxide (NO) by injection of plasma-produced reactive agents. As reactive agents we tested ozone (O₃), NH and NH₂ radicals from ammonia (NH₃) and nitrogen atoms (N) generated in dielectric barrier discharges (DBDs) as well as hydrazine (N₂H₄) as a reducing agent and direct plasma treatment of the entire exhaust gas was investigated. We performed laboratory experiments on synthetic exhaust gases, modelling of the mechanisms and a demonstration of the technique on a test engine, a 30 kW combustion engine fuelled with natural gas.

We achieved the best results with ozone injection into the exhaust gas. This technique is based on oxidation of NO to N₂O₅ that is subsequently removed from the exhaust gas by a scrubber. In the laboratory experiments we obtained complete removal of NO by injection of an ozone/oxygen mixture from an oxygen (O₂) DBD into synthetic exhaust gases with compositions close to those of real exhaust gases.

Ozone injection was chosen for demonstration of NO_x removal from the exhaust gas of the test engine. We achieved 95 % NO_x removal with an oxygen DBD and 70 % NO_x removal with an air DBD. The running costs relating to the demonstration were estimated to be approximately 30 DKK per kg removed NO_x for the oxygen DBD, and 25 DKK per kg removed NO_x for the air DBD.

For a commercially available ozone generator, the total costs of NO_x removal from a 3 MW power plant were estimated to 27 DKK per kg removed NO_x for oxygen as the feed gas, and 21 DKK per kg removed NO_x for air as the feed gas.

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Preface

In this report the work performed during the PSO project no. FU3401 “Emission reduction from combustion engines by means of low temperature plasmas” is summarised. Details about the final stage of the project, i.e. demonstration of NO_x removal at the 30 kW test engine, are available in Appendix 1 (Description of the experimental setup for NO_x reduction by O₃ – Danish Gas Technology Centre), Appendix 2 (NO_x removal experiments at the engine) and Appendix 3 (NO_x emission control using low temperature plasma, economical evaluation – Danish Gas Technology Centre). Details about the initial laboratory experiments can be found in the 3 status reports for the project covering the periods 1 June to 31 December 2003, 1 January to 31 June 2004 and 1 July to 31 December 2004.

The project was carried out as a collaborative project between Risø National Laboratory (Risø) and the Danish Gas Technology Centre (DGC) running from 1 June 2003 to 31 July 2005. The initial laboratory experiments were carried out at Risø. The demonstration of NO_x removal was performed at the test engine located at DGC.

Bjarne Sass, Martin Jessen and Søren Nimb from Risø and Johan G. Larsen from DGC are gratefully acknowledged for their technical assistance during the project. Bitten Skaarup from Risø and Conny R. Petersen from DGC are gratefully acknowledged for their editorial support.

Final report for PSO project no. FU3401

The work performed during the PSO project no. FU3401 “Emission reduction from combustion engines by means of low temperature plasmas” is summarised below. In this project we studied removal of toxic gaseous emission from combustion engines by mixing the exhaust gases with reactive agents generated in low temperature plasmas. We focused on removal of nitrogen oxides N_xO_y (NO , NO_2 , NO_3 , N_2O_5 and N_2O) and, in particular, on removal of nitrogen monoxide (NO).

The studies were carried out as laboratory studies, modelling of the chemical reaction paths and demonstration of NO_x removal from the exhaust gas of a test engine. For the laboratory experiments we established diagnostics and gas handling facilities for mixing of the synthetic exhaust gases and the gas mixtures fed to the plasma generators. For some of the initial laboratory studies we used a mixture of nitrogen (N_2) and NO (500 ppm) as a standard synthetic exhaust gas. This mixture was also used as the base for producing more realistic synthetic exhaust gases. Optical spectroscopy was used for diagnostics. A deuterium lamp with ultraviolet (UV) emission and a spectrometer equipped with a CCD camera were used for the UV absorption spectroscopy measurements. The spectrometer was also used for emission spectroscopy. Fourier transform infrared (FTIR) spectroscopy was employed for infrared (IR) absorption measurements. For the demonstration at the test engine, the NO_x concentration was measured with a calibrated chemiluminescence NO_x analyzer.

We tested two different techniques for NO_x removal by means of low temperature plasmas. In *remote treatment*, a reactive agent is generated in a low temperature plasma and injected into the exhaust gas. In *direct treatment*, the entire exhaust gas is exposed to the plasma. The plasmas were generated in dielectric barrier discharges (DBDs). Basically, a DBD consists of two metal electrodes covered with dielectric barriers, typically alumina (Al_2O_3). DBDs are AC powered, typically 10 – 20 kV at frequencies of 10 - 40 kHz. The input powers were determined by voltage and current measurements. At high power inputs the electrodes were water-cooled. During the project several DBDs with different geometries have been constructed and tested. Normally the DBDs were operated at atmospheric pressure. A DBD with parallel plate electrode geometry was placed in a sealed chamber equipped with optical windows for diagnostics of the plasma. In oxygen DBDs with coaxial electrodes, ozone could be produced in concentrations up to approximately 7 vol %.

As reactive agents we tested plasma-generated ozone (O_3), NH and NH_2 radicals from ammonia (NH_3) and nitrogen atoms (N). In addition, we investigated injection of hydrazine (N_2H_4) and direct plasma treatment. We used ozone injection into the exhaust gases for the demonstration at the test engine since the laboratory studies with ozone injection have given the most promising results.

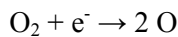
Recently, a commercial system applying ozone injection has become available under the trademark LoTOx (see, e.g., “Using Non-Thermal Plasma to Control Air Pollutants”, United States Environmental Protection Agency, EPA-456/R-05-001, February 2005, www.epa.gov/ttn/catc/dir1/fnonthrm.pdf).

1 Remote treatment

1.1 Injection of ozone

NO_x removal by ozone injection takes place as oxidation of NO_x to N₂O₅ and subsequent removal of N₂O₅ by a scrubber. In an O₂ DBD, ozone is formed according to the following reactions:

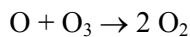
Dissociation by electron impact:



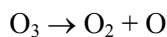
and a subsequent formation of ozone (where M is a third body):



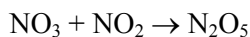
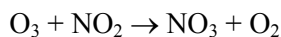
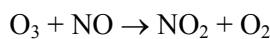
At steady state the ozone production is balanced by the decomposition reactions:



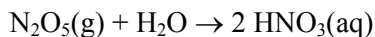
and thermal dissociation:



In, for example, an exhaust NO can be oxidized by O₃ to form NO₂, NO₃ and, subsequently, N₂O₅:



The oxidation of NO₂ to NO₃ is the slowest reaction in this chain. N₂O₅ can be efficiently removed from the exhaust by a washing bottle or a scrubber according to the following reaction forming nitric acid (HNO₃):



In humid exhaust gases, HNO₃ may be formed in the exhaust gas itself.

1.1.1 Laboratory experiments on ozone injection

In the laboratory studies we tested NO removal by injection of ozone into synthetic exhaust gases at various ozone concentrations and various temperatures of the exhaust gas. We used an atmospheric pressure O₂ DBD with parallel plate geometry for the ozone production. As synthetic exhaust gases we used N₂/O₂/NO/CH₄ mixtures with compositions close to those of real exhaust gases. Some experiments were carried out with water vapour in the exhaust gas as well. The water vapour was introduced by means of an electronically controlled evaporator.

The experiments were performed in a quartz tube in order to reduce the influence of surface reactions. The quartz tube with inlets for the synthetic exhaust gas and for the O_2/O_3 mixture from the DBD was placed in a furnace. After a residence time of 3 - 4 s the mixture passed a washing bottle. The time required for the oxidation to complete was estimated to be about 2 s at room temperature (the time required to oxidize 63 % ($1/e$ decay) of the initial NO_2 in a 500 ppm O_3 environment). The exhaust gases with and without passing the washing bottle were analysed by UV and IR absorption spectroscopy.

UV absorption spectroscopy showed that NO could be removed completely from the tested synthetic exhaust gases and that the final product in the washing bottle was HNO_3 . This indicates that the oxidation from NO to N_2O_5 took place. When the O_3 supply was insufficient, the oxidation from NO to N_2O_5 could not be completed. It was found that the washing bottle could not trap NO_2 efficiently.

The NO removal was efficient at temperatures below 120 °C. At temperatures between 120 °C and 250 °C, the NO removal efficiency dropped and above 400 °C no NO removal was observed.

1.1.2 Ozone injection at the 30 kW test engine

The final stage of the project was a demonstration of NO_x removal from the exhaust gas from the test engine at DGC by ozone injection. The total exhaust gas flow rate from the engine was 2400 standard litre per minute (SLM). The NO_x concentration in the exhaust was normally between 300 and 700 ppm. A side tube with about 10 % of the total exhaust (250 SLM) was used for demonstration of NO_x removal. A prototype plasma source (a large coaxial DBD) for ozone generation was designed as well as a scrubber system for trapping N_2O_5 and HNO_3 . The source was tested at Risø in advance in order to optimize the condition.

The nozzles for injection from the DBD were designed to guarantee fast and efficient mixing of the gases. The reaction chamber allows a reaction time of about 3 s for the oxidation of NO to N_2O_5 .

UV/IR absorption spectroscopy and the chemiluminescence NO_x analyzer available at DGC were used for detection of nitrogen oxides after ozone injection, after mixing and at the exhaust. The ozone concentration in the outlet of the DBD was measured by means of laser absorption at 634.7 nm, while ozone at the scrubber outlet was detected by UV absorption.

Pure oxygen, air and synthetic air (80 % N_2 + 20 % O_2) were used as feed gases for the DBD. Tests of oxygen as feed gas were performed at exhaust gas temperatures about 160 °C and about 110 °C. The NO_x concentration in the exhaust after the scrubber outlet was measured with the chemiluminescence NO_x analyzer. The NO_x emission decreased with increasing DBD power input and oxygen flow rate. This is a result of a higher ozone production rate at high DBD powers and oxygen flow rates. At exhaust gas temperatures of 160 °C, an NO_x removal of about 95 % was achieved at an oxygen flow rate of 6 SLM and a DBD power input of 390 W. At 110 °C, 95 % NO_x removal was obtained at an oxygen flow rate of 3 SLM and a power of 250 W. The experiments performed with compressed air at about 140 °C showed maximum NO_x removal efficiency of about 70 % at a flow rate of 35 SLM and a DBD power of 500 W. Humidity is known to reduce the O_3 production and synthetic air was found to be more efficient and showed NO_x removal efficiency up to 90 %.

It should be noted that nitrogen oxides may be produced in an air DBD and that N_2O produced in the DBD cannot be removed at a later stage. It was found that the emission of N_2O was of the order of 2 – 5 ppm at the scrubber outlet. There is no production of nitrogen oxides in oxygen DBDs.

IR absorption spectroscopy measurements at different positions downstream the reaction chamber indicate that the oxidation took place on a time scale considerably shorter than the 3 s expected at room temperature. However, the time of transportation of the exhaust to the FTIR spectrometer may allow further reactions before the analyses were performed. At a temperature of 125 °C the reaction time is approximately a factor of 10 shorter than that at 25 °C, and it seems likely that the oxidation is almost completed at the inlet of the reaction chamber.

Measurements of the ozone concentration in the injected O_2/O_3 mixture showed that the O_3 consumption for the NO_x removal was comparable with that expected from the stoichiometry of the oxidation of NO to N_2O_5 , and it is unlikely that the ozone consumption can be reduced significantly. However, compared with the energy required to dissociate the oxygen molecules, the energy consumption for the ozone production is large indicating that the power consumption may be reduced. The total power consumption at 95 % NO_x removal corresponds to about 15 % of the total power from the engine for ozone generation from oxygen (110 °C, O_2 flow rate of 3 SLM, DBD power of 250 W) and to about 30 % for ozone generation from air with 70 % NO_x removal (140 °C, air flow rate of 35 SLM, DBD power of 500 W).

For oxygen as feed gas, the running costs of the demonstration were estimated to be about 30 DKK per kg removed NO_x at a removal efficiency of 95 % (110 °C, O_2 flow rate of 3 SLM, DBD power of 250 W). The running costs are dominated by the costs of the oxygen consumption of about 20 DKK per kg removed NO_x . For air as DBD feed gas, the running costs were estimated to be about 25 DKK per kg removed NO_x at a removal efficiency of 70 % (140 °C, air flow rate of 35 SLM, DBD power of 390 W). (For the cost estimations the NO_x emission is considered as NO_2 emission, and an oxygen price of 1.20 DKK/ Nm^3 , a compressed air price of 0.03 DKK/ Nm^3 and a local price for the power of 0.20 DKK/kWh have been assumed).

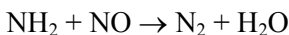
The DBD ozone generator used for the test engine was not optimized with respect to costs and energy efficiency. For a commercially available ozone generator the power consumption corresponds to 8 % of the power of the power plant (3 MW) for 95 % NO_x removal with oxygen as feed gas or for 70 % NO_x removal with air as feed gas.

For the commercially ozone generator the total costs incl. the capital costs were estimated to

- 27 DKK per kg removed NO_x for 95 % removal for ozone generation from oxygen
- 21 DKK per kg removed NO_x for 70 % removal for ozone generation from air (8 DKK per kg removed NO_x for the air consumption). For ozone generation from air the capital costs are a factor of two larger than for ozone generation from oxygen.

1.2 Injection of NH₂ radicals

Initially, we studied reduction of NO in exhaust gases by injection of NH₂ radicals produced in argon/ammonia (Ar/NH₃) DBDs according to the reaction:



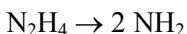
Several DBD geometries were tested with powers up to several hundreds of watts and with ammonia concentrations up to about 10 %. The plasma and the reactive species were analysed with emission and absorption spectroscopy. Strong emission from NH radicals was observed, but NH₂ radicals could not be detected by emission spectroscopy most likely due to strong quenching of the excited level of the NH₂ radicals. Ground state NH₂ radicals were detected by laser absorption spectroscopy. The highest NH₂ concentration was found for an NH₃/Ar concentration between 6 % and 8 %, but absolute NH₂ concentrations could not be measured with this technique. Modelling indicates that the main stable products of an Ar/NH₃ plasma are nitrogen molecules (N₂), hydrogen molecules (H₂) and hydrazine (N₂H₄) and that the concentration of NH₂ is low due to a short lifetime (0.3 ns). NH₂ is expected to recombine to N₂H₄ which was detected by UV absorption spectroscopy in the plasma as well as in the exhaust gas.

Injection from an Ar/NH₃ (6 %) plasma into synthetic exhaust gas (standard N₂/NO mixture) showed a small NO reduction at room temperatures. At 340 °C the NO reduction was more efficient than at room temperature. This may be assigned to thermal decomposition of N₂H₄ or catalytic reactions on heated stainless steel surface (see below).

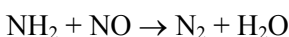
Ar is costly and not very efficient as carrier gas and nitrogen (N₂) was tested instead. Comparisons of Ar and N₂ as carrier gases indicated that the production rate of NH₂ radicals in an N₂/NH₃ plasma was comparable with that in the Ar/NH₃ plasma. Injection from N₂/NH₃ plasmas into synthetic exhaust gas (standard N₂/NO mixture) showed some NO reduction. However, the most efficient reduction was observed with injection from pure N₂ plasmas. This reduction is assigned to injection of N atoms (see below).

1.3 Injection of hydrazine

As mentioned in the previous section one of the products in Ar/NH₃ and N₂/NH₃ DBDs is N₂H₄. Thermal dissociation of N₂H₄ into NH₂ radicals takes place at temperatures above 300 °C:



The NH₂ radicals may promote NO reduction:



At room temperature N₂H₄ is stable and can therefore be injected into the hot exhaust gas.

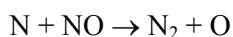
Tests with injection of hydrazine into heated synthetic exhaust gas (standard N₂/NO mixture) were performed in order to investigate the applicability of N₂H₄ as a reducing agent. The experiments were performed in a quartz tube placed in a

furnace. No significant NO reduction was observed at exhaust gas temperatures below 700 °C while hydrazine decomposes at temperatures above 300 °C. Ammonia was found to be the main product of the decomposition. Experiments with a heated stainless steel tube suggested that catalytic surface reactions significantly interfere with gas phase reactions.

It was concluded that N₂H₄ cannot be used for NO reduction at temperatures below 700 °C.

1.4 Injection of nitrogen atoms

N atoms generated in N₂ DBDs have shown to reduce NO according to the reaction:



However, the lifetime of the N atoms is short. Different DBDs have been designed in order to reduce the transportation time of the N atoms from the plasma to the exhaust. The NO reduction in synthetic exhaust gases (standard N₂/NO mixture) was monitored by means of UV absorption spectroscopy and FTIR spectroscopy. The strongest NO reduction was observed with short distances from the DBD to the mixing volume and high injection flow rates. At an injection, a flow rate 6 times the flow rate of the synthetic exhaust gas up to 75 % NO reduction was observed. For an N₂ flow rate equal to the flow rate of the exhaust, a maximum reduction of 28 % was achieved. The high injection flow rate is required due to a low concentration of nitrogen atoms in the mixing volume between the injected plume and the exhaust gas. The recombination of N atoms is so fast that it seems unrealistic to achieve high concentration of N atoms in the mixing volume.

It was concluded that the technique is too expensive, although NO reduction as the result of injection of nitrogen atoms was observed.

2 Direct treatment

Some tests of direct treatment of the synthetic exhaust gases were performed in order to investigate whether N atoms generated from the N₂ in the exhaust gas could reduce NO. In the first tests with the standard exhaust gas fed to a coaxial DBD, the NO concentration was reduced 93 %. However, the total N_xO_y concentration was 14 % of the initial NO concentration indicating that both reduction and oxidation of NO took place. In synthetic exhaust gas mixtures of O₂ (7 %), N₂ and NO (465 ppm), the NO concentration could be reduced slightly, but the total concentration of N_xO_y increased with power up to a maximum of about 850 ppm. Even in the absence of NO in the synthetic exhaust gas, considerable amounts of N₂O were detected after plasma treatment. Experiments performed using humid exhaust gases (the exhaust gas passed a washing bottle with water before treatment) showed that humidity promotes the N_xO_y production even in the absence of O₂ in the synthetic exhaust gases. The total N_xO_y concentration was found to increase slightly by adding NH₃ to the exhaust gas. The experiments with the coaxial DBD were performed without preheating of the exhaust gases. However, the gases were heated in the DBD.

Some experiments were performed with humid (about 1 %) synthetic exhaust gases (N₂/O₂ (7 %)/NO) preheated to about 40 °C. The gases were fed to the DBD with parallel plate electrodes, and minor additional plasma heating of about 10 °C could be expected. Although humidity was found to promote NO production, a complete

NO removal was obtained by adding methane CH_4 (6 %) to the synthetic exhaust gas. However, if methane (or other hydrocarbons) is present in the discharge, production of toxic compounds for example CN compounds is possible.

Although direct treatment of the exhaust is being used and high energy efficiency has been reported, we have concluded that direct treatment of the exhaust gas is not suitable for this project. At our experimental conditions we did not observe efficient N_xO_y reduction at low methane concentration.

Appendix 1

Description of the experimental setup for NO_x reduction by O₃

This technical note describes the experimental setup for reduction of NO_x in the exhaust from a test engine by O₃ produced in a Dielectric Barrier Discharge (DBD). The experimental setup is located at the laboratory at the Danish Gas Technology Centre.

1. Test engine

The test engine is a Ford 4-cylinder, 4-stroke diesel engine with a displacement of 4.15 litres rebuilt for lean-burn operation on gas. The compression ratio is 11:1, the air intake is assisted by a turbocharger and the engine is equipped with an ignition system. The engine has a single gas carburettor mounted before the turbocharger.

The gas supply to the carburettor has a mixer for operation on air-natural gas mixtures and the fuel-air ratio can be adjusted manually during operation. The coolant is heat exchanged with water and the heat is dissipated in a cooling tower.

The turbocharger has a charge pressure regulation. This allows maintaining a constant power output during operation with different fuel-air ratios. By using a higher charging pressure at lean operation, the output power can be maintained at the same level.

2. Exhaust system

The exhaust system consists of thermally insulated metal pipes and flex pipes. The exhaust gas exits the engine through the manifold and enters the thermally insulated H-shaped pipe segment. The pipes in this segment are made of metal pipes (55x2.5). This segment leads the exhaust gas to the turbo charger and from there it passes through a segment of flex pipe. The flex leads to the wall of the engine room. Through the wall and into the last pipe segment the pipe system is made of metal pipe (60.3x2).

Figure 1 shows a schematic drawing of the engine room and exhaust system. All pipes include the heat insulation material. Green arrows indicate the exhaust gas flow through the pipes.

Description of the experimental setup

From the engine room the exhaust is passing through a cooling system. The four valves are used for adjusting the flow rate through the exhaust system and through the NO_x reduction system.

The NO_x reduction system starting with the pipe to the DBD introduces a back pressure, i.e. there is a pressure drop through the NO_x reduction system. This back pressure has to be balanced by adjusting the four valves around the cooling system. The valves are also used to adjust the cooling of the exhaust to the NO_x reduction.

The flow rate of exhaust from the engine is about 2500 l_n/min. The flow rate through the NO_x reduction system is approximately 250 l_n/min.

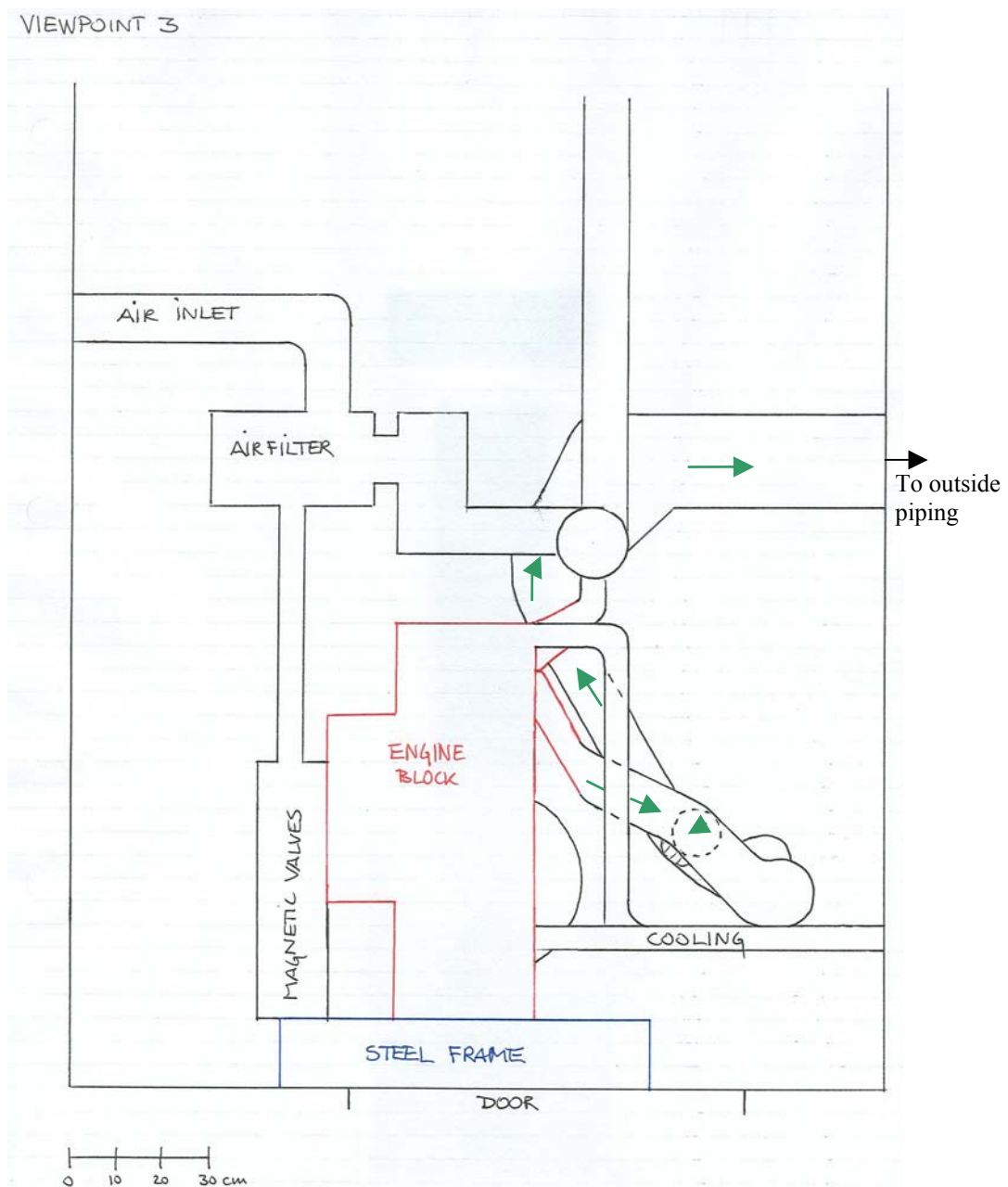


Figure 1. Schematic drawing of the engine room.

The DBD produces ozone (O_3) in a low temperature atmospheric pressure plasma. The ozone concentration varies between 2 and 7 % (volume), depending on the discharge power and oxygen supply flow rate. The O_2/O_3 mixture is mixed with the experimental part of the exhaust. A mixing device was constructed for the best possible mixing at the mixing point. This is described in the following section.

The mixing system was designed to achieve a fast mixing of the injected O_2/O_3 mixture with the exhaust gas in order to achieve the best possible conditions for the reaction. The designed system can be seen in Figure 3.

The design is optimised in order to have maximum turbulence with 6 l/min of O_2/O_3 mixture injected into approximately 250 l/min of exhaust gas. It is estimated that the mixing is complete within 0.050 seconds.

After the mixing the mixture passes through the reactor with a volume of 23 litres in which the chemical reaction between ozone and NO_x was supposed to take place (the reaction was much faster than anticipated and most of the reactions took place before the reactor).

In the chemical reactions NO_x is oxidized to N_2O_5 which is soluble in water. The mixture is guided to a scrubber in which the N_2O_5 is washed out. The volume of the scrubber is about 42 litres. The scrubber is filled with plastic filling material which creates a large surface for the washing of the mixture. The scrubber is designed for a larger gas flow than used in the experiments.

The cleaned mixture from the scrubber passes an orifice meter to measure the flow rate of the mixture. This orifice meter creates a backpressure on the system which is balanced by the valves around the cooling system as mentioned above. From here the mixture flows to the exhaust exit.

The orifice meter was constructed and made for the purpose of this project. The meter was calibrated against a reference flow meter. The volume flow was found to be:

$$V = 50 (\Delta p / \rho)^{0.5}$$

V (volume flow in l/min), Δp (differential pressure in mbar), ρ (density in kg/m^3). The uncertainty is about 5%.

The water in the scrubber flows in a closed system for this experimental purpose. After the scrubber a pH-meter measures the acidity of the water. The water flows to a tank of about 500 litres. A pump and a flow meter for the water are used to adjust the water flow to about 10 l/min. A spray above the filling material creates a good distribution of the water in the scrubber.

In Figure 2 the points where measurements of temperatures and concentrations are performed are marked with numbers. At point (4) the development through the reactor can be measured. Measuring point (3) is about 0.05 sec downstream from mixing point. Points 4a, 4b, 4c and 4d are approximately 0.5, 1, 2 and 3 sec of residence time downstream from mixing point.

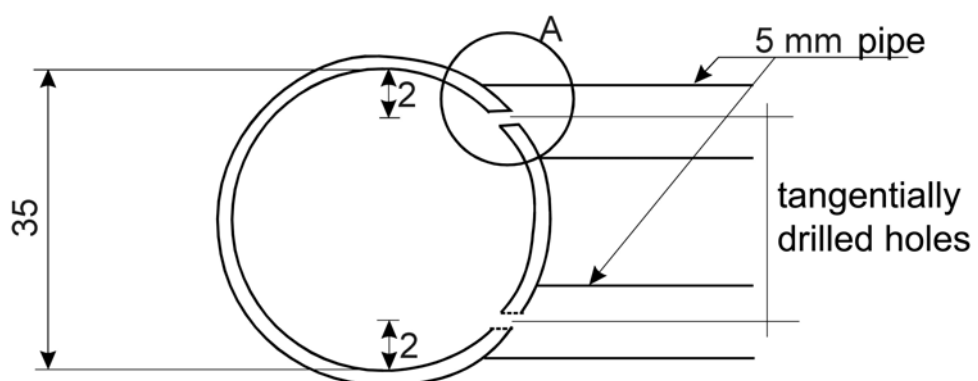
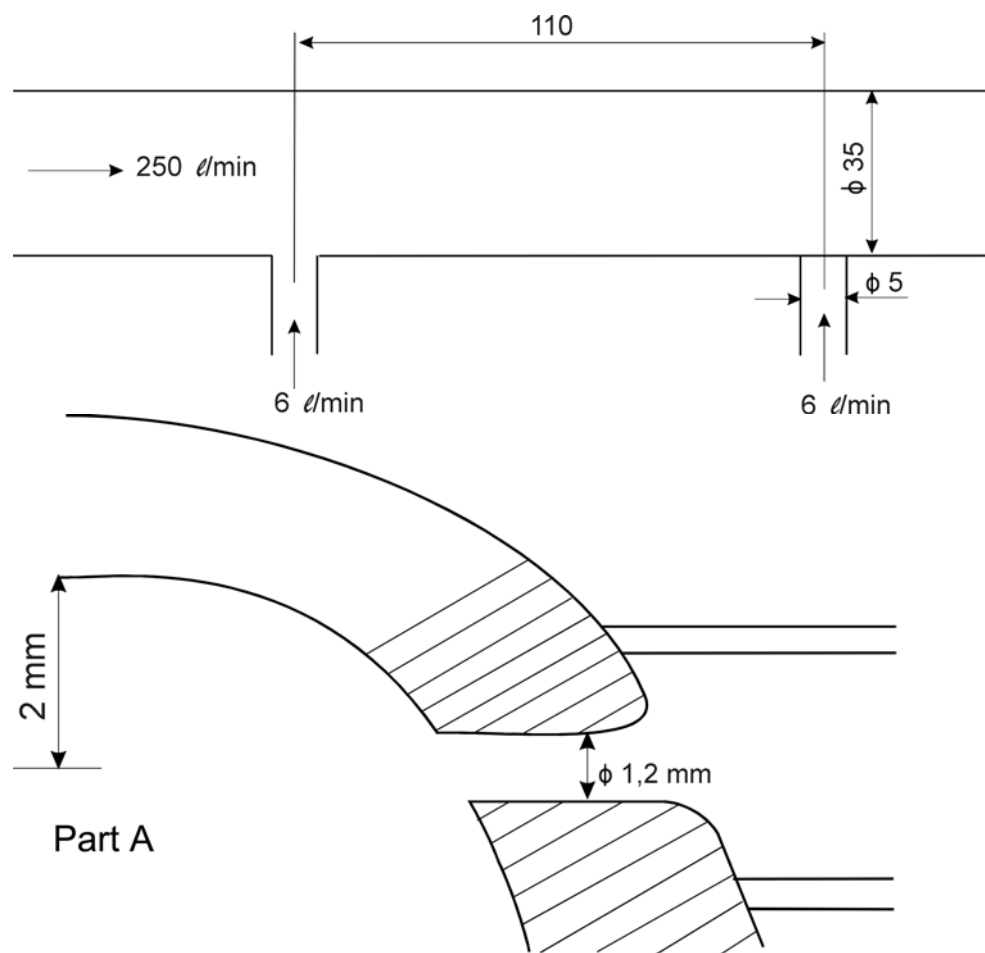


Figure 3. *Mixing system.*

The plasma source

For these experiments, an atmospheric pressure DBD with coaxial electrode geometry was used. An Al_2O_3 cylinder between the electrodes serves as a dielectric barrier. A schematic of the DBD is shown in Figure 4. Both electrodes were water cooled. The water flow is depicted blue in Figure 4. The discharge was between the outer surface of the ceramic and the outer adjacent metal cylinder. The oxygen flow parallel to the axis is also the plasma volume, depicted red in Figure 4. The DBD is driven by an AC power supply.

For continuous (cw) operation, the power supplied to the DBD was adjusted by changing the frequency in the range between 20 kHz and 40 kHz corresponding to a power up to 1500 W. In order to apply lower powers, the power supply was operated in pulsed mode. The pulse consists of one full sinusoidal period (54.65 μs) of high voltage followed by a pause of adjustable duration. The power supplied to the DBD is the average power. This is the energy provided in one pulse divided over the repetition time.

Voltage and current were measured by means of a high voltage probe and a current viewing resistor, respectively. The average power input was obtained by multiplying voltage and current numerically and integrating over one AC period.

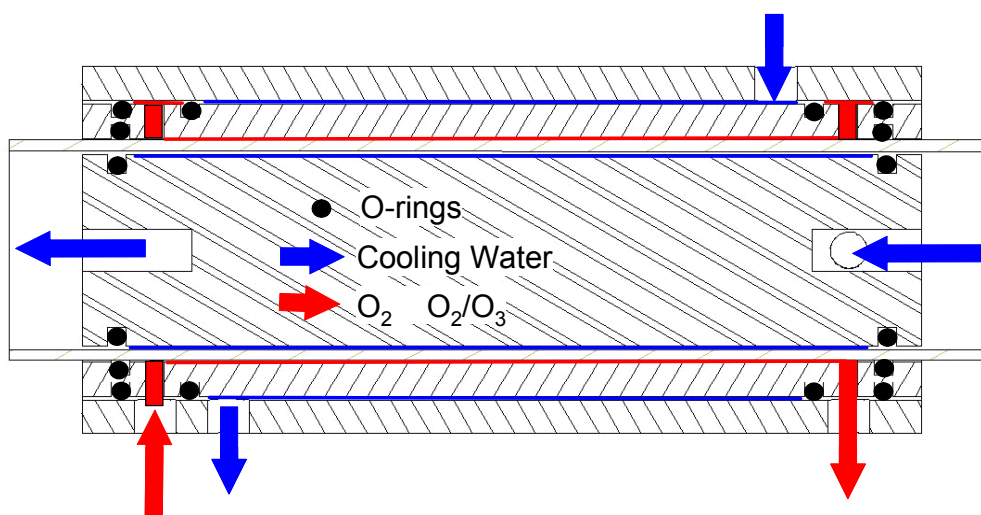


Figure 4. DBD.

The oxygen is fed to the inlet in Figure 4. The O_2/O_3 mixture leaves the discharge to the outlet. Both are depicted as red arrows in Figure 4. The O_2 flow rate can be varied from 1 l/min to 16 l/min. the O_3 concentration depends on the flow rate and power input and varies between 2.7 and 7 vol %.

O_3 detection

The ozone concentration at the outlet of the DBD was measured by means of laser absorption spectroscopy. Ozone has an absorption band in the visible with a maximum at 600 nm. The absorption was measured with a diode laser at 634.7 nm, where the absorption cross section is approximately 60% of the maximum cross section.

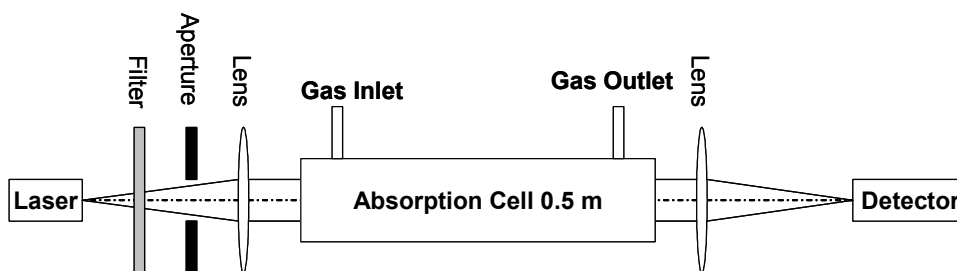


Figure 5. Diagnostic for ozone concentration measurement.

A sample of the outlet gas of the DBD is guided in the absorption cell Figure 5. The light intensity at the detector is measured by means of a photo diode. The reference light intensity is obtained when the plasma is off. Ozone concentrations between 0.5 % and 10 % can be measured with this setup.

NO, NO₂ N₂O detection

Nitrogen oxide were measured by means of a FTIR (Fourier transform infrared spectroscopy)

NO, N₂O₅ detection

NO and N₂O₅ have absorption bands in the UV and can therefore be detected by means of UV absorption. The experimental setup is depicted in Figure 6.

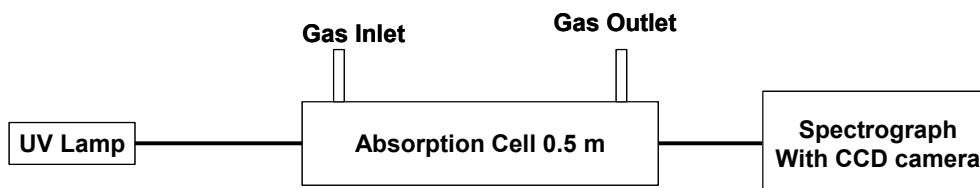
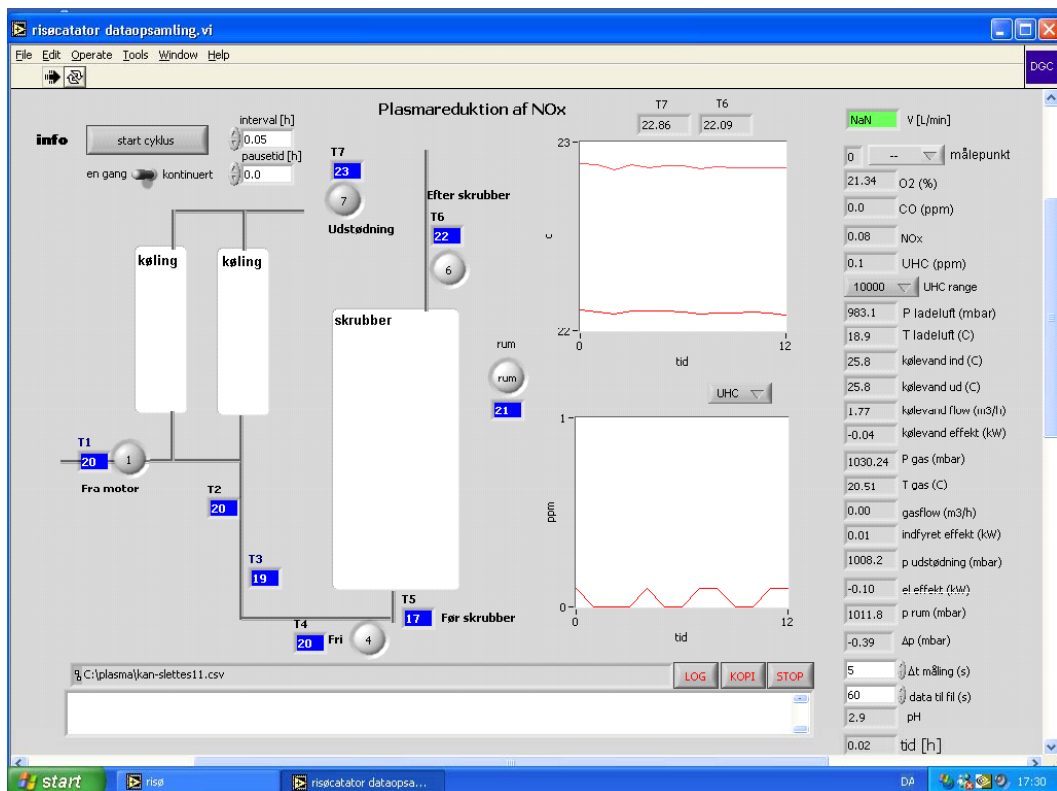


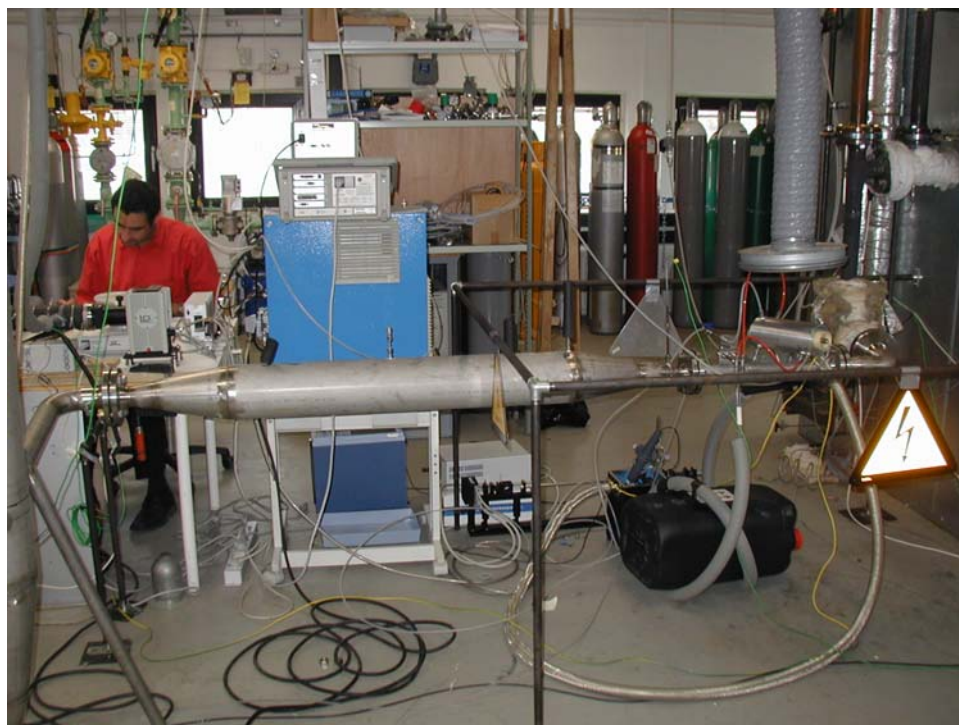
Figure 6. UV absorption spectroscopy.

Pictures of the setup

On the next pages some pictures show the experimental setup.



Picture 1 A screen dump from the screen of the data collection system.



Picture 2. The important parts of the experimental setup. On the right the ozone generator (DBD). On the left the reactor and behind the power supply and O₂ supply for the DBD.



Picture 3. A closer look at the ozone generator.



Picture 4. On the left the scrubber and behind it the water tank.



Picture 5. On the right the copper cooling coil for water cooling of the exhaust system.



Picture 6. A close up of the ozone generator.

Appendix 2

NO_x removal experiments at a DGC laboratory gas engine

1 Introduction

The final stage of the project was demonstration of NO_x removal from the exhaust gas of a 30 kW natural gas driven combustion engine located at DGC. The total exhaust gas flow rate of this engine was 2400 standard litre per minute (SLM). The NO_x concentration in the exhaust was between 300 and 700 ppm. About 10 % of the gas stream (250 SLM) was treated by ozone generated from oxygen or air in a dielectric barrier discharge (DBD). The experimental set-up (plasma generator, reaction chamber and a scrubber system) is described in detail in Appendix 1 (Description of the experimental set-up for NO_x reduction by O₃).

The ozone generated in the DBD is transported to the mixing volume where the oxidation of NO to N₂O₅ occurs. The nozzles for injection from the DBD were designed to guarantee fast and efficient (turbulent) mixing of the gases. In the reaction sequence $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$, the oxidation of NO₂ to NO₃ is the slowest process. The decay of NO₂ (due to oxidation to NO₃ with O₃) to 1/e of its initial concentration takes 2.2 s in a 500 ppm O₃ environment at room temperature. The reaction chamber allows a reaction time of about 3 s comparable with that used in the laboratory experiments. N₂O₅ can be efficiently removed by a scrubber system forming nitric acid. Experiments with pure oxygen, air and synthetic air (80 % N₂ + 20 % O₂) as feed gas for the DBD were carried out.

UV/IR absorption spectroscopy and a chemiluminescence NO_x analyzer available at DGC were used for detection of nitrogen oxides after ozone injection, after mixing and at the exhaust. UV absorption was also used to detect NO₃⁻ in water. The ozone concentration in the outlet of the DBD was measured by means of laser absorption at 634.7 nm, while ozone measurements at the scrubber outlet were measured by UV absorption.

2 Experiments with O₂ as feed gas for the DBD

The first measurements of NO_x removal were performed with oxygen as the DBD feed gas. The temperature of the exhaust gas in the mixing volume was about 160 °C. The exhaust gas was additionally cooled downstream the reaction chamber. During operation, water condensation at the bottom of the reaction chamber was observed. UV absorption measurements showed that this water contained NO₃⁻ ions which indicates that N₂O₅ is formed in the reaction chamber. Figure 1 shows the NO_x concentration in the exhaust gas measured after the scrubber at various settings of the DBD power and oxygen flow rates through the DBD. The NO_x emission is decreasing with increasing power input to the DBD and with increasing oxygen flow rate. This is a result of higher ozone production rates at high DBD powers and high oxygen flow rates. Depending on the NO_x concentration in the exhaust gas, various oxygen-ozone flow rates are required to remove the NO_x. If the ozone flow rate is too low, the oxidation from NO to N₂O₅ will not be completed. If the ozone flow rate is too high, ozone will be present in the exhaust gas. At an oxygen flow rate of 6 SLM and a DBD power input of 390 W, the NO_x removal efficiency was about 95 %. At higher DBD powers, ozone was detected after the scrubber by UV absorption spectroscopy.

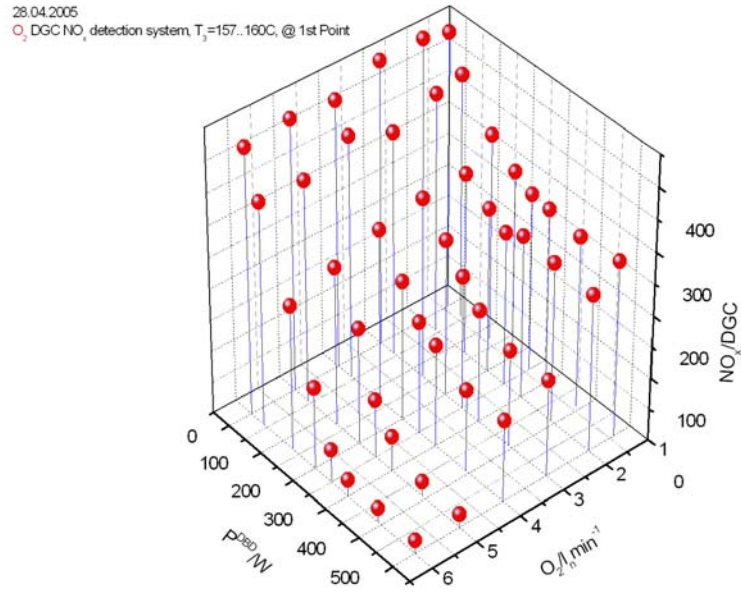


Figure 1. NO_x concentration in exhaust after the scrubber measured with the chemiluminescence NO_x analyzer versus power settings and oxygen flow rates. The mixing temperature was about 160 °C.

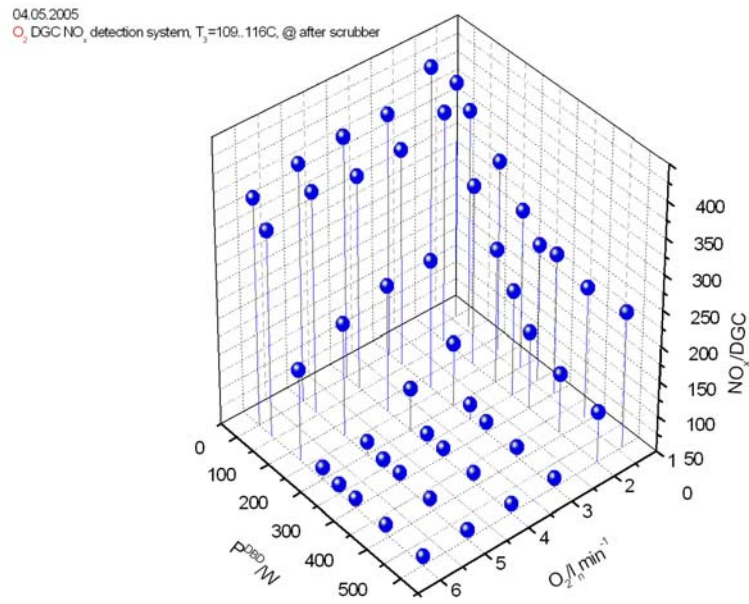


Figure 2. NO_x concentration in exhaust after the scrubber measured with the chemiluminescence NO_x analyzer versus power settings and oxygen flow rates. The mixing temperature was about 110 °C.

Experiments were carried out with the exhaust gas cooled down to a temperature of about 110 °C in the mixing volume as well. In order to prevent condensation of water, the temperature was kept above 100 °C in the mixing volume. The measurements at 110 °C were performed with the same settings of the DBD power and the O₂ flow rate as those used for the measurements at 160 °C. Figure 2 shows the NO_x concentrations measured at the scrubber outlet versus discharge power and oxygen flow at a mixing temperature of 110 °C. 95 % removal was achieved at an oxygen flow rate of 5 SLM and a power consumption of 250 W showing that the removal efficiency is improved compared with that at 160 °C. The decomposition rate of ozone is decreasing with decreasing temperature.

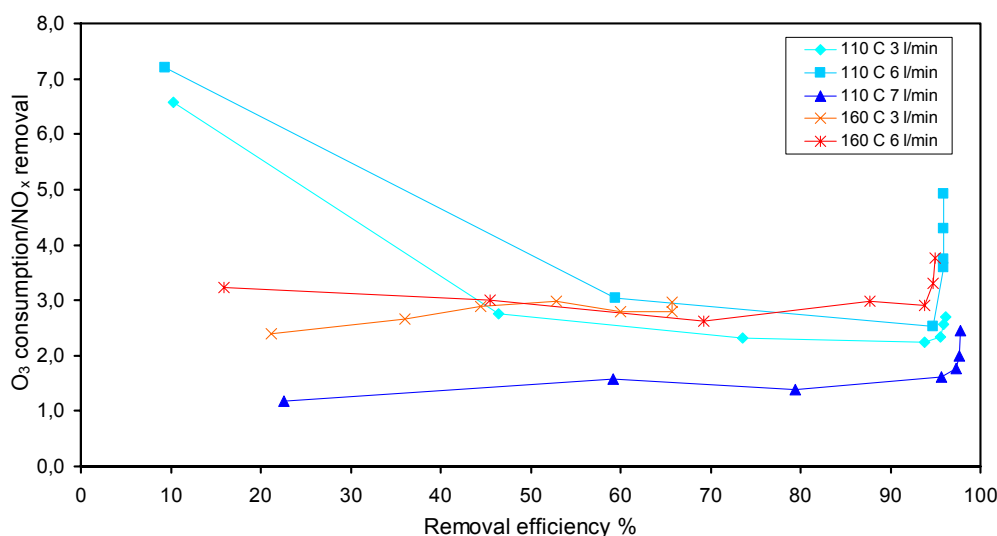


Figure 3. The ratio of the O₃ consumption to the amount of removed NO_x (O₃ consumption/NO_x removal).

Measurements of the ozone concentration in the O₂/O₃ mixture show that the O₃ consumption for the NO_x removal is comparable with that expected from the stoichiometry of the oxidation of NO to N₂O₅. Experimentally the ratio of the O₃ consumption to the amount of removed NO_x ranges from 1.4 up to 7 (Figure 2). For pure NO emission the lowest achievable ratio is expected to be 1.5 while it is expected to be 0.5 for pure NO₂ emission. The measurements of the ozone consumption indicate that the ozone consumption cannot be reduced significantly. The ozone consumption is low at a mixing temperature of 110 °C and an oxygen flow rate of 7 SLM. These measurements were performed at a high initial NO_x concentration of about 660 ppm. Close to a removal efficiency of 100 % the ratio of the O₃ consumption to the amount of removed NO_x ratio is increasing. This can be explained by the release of ozone from the scrubber detected by UV absorption.

In order to investigate the dynamics of the NO_x oxidation, IR-absorption measurements at different points between the injection point and the scrubber outlet were performed. Figure 4 shows the IR spectra of the exhaust gas without treatment, at the inlet to the reaction chamber and after the scrubber system, respectively. No significant difference between the spectrum after the mixing volume and that after the scrubber system can be observed which indicates that the oxidation of NO to N₂O₅ mostly takes place in the ozone injection volume. However, the time of transportation of the exhaust gas to the FTIR spectrometer may allow further reactions before the analyses were performed. The rate constant for the reaction NO₂ + O₃ → NO₃ + O₂ at 125 °C is 9.4 times higher than that at 25 °C, and it seems likely

that the oxidation is almost completed at the inlet of the reaction chamber. For an exhaust gas flow rate of 250 SLM and the rate constant for the oxidation of NO_2 to NO_3 at 125 °C, the NO_2 decays to 1/e of its initial concentration within 50 cm travel path in the exhaust pipe.

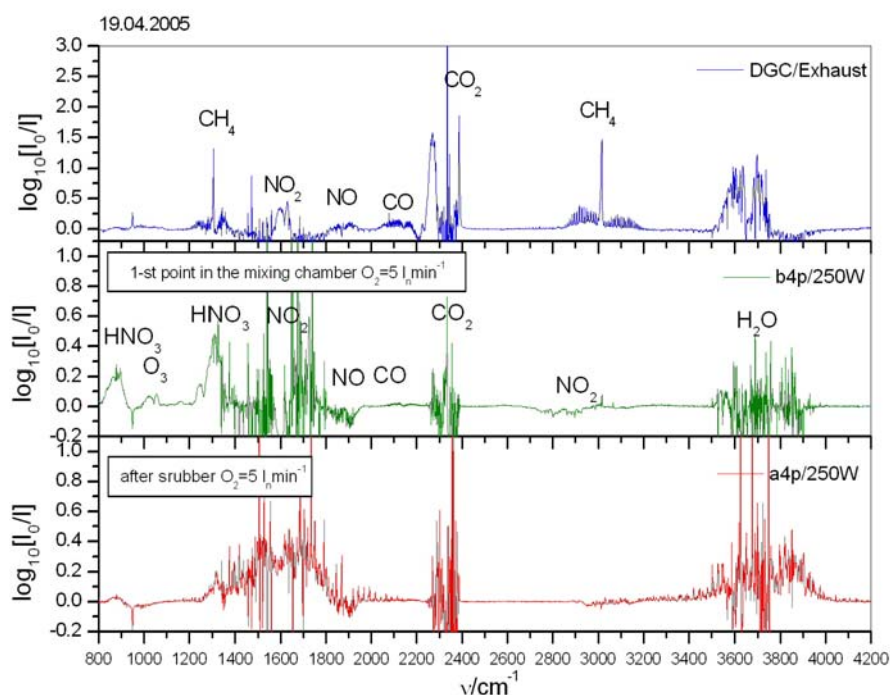


Figure 4. Typical IR absorption spectra of the untreated exhaust gas, after O_3 treatment measured at the inlet to the reaction chamber and after the scrubber. The concentration of NO_x after engine was 700 ppm. The mixing temperature was 160 °C, the O_2 flow rate was 5 SLM and the DBD power was 250 W.

3 Experiments with air as feed gas for the DBD

Ozone can be produced in an air DBD. However, the ozone concentration is lower than that in a pure oxygen fed DBD, and higher power inputs and gas flow rates are required in order to produce the same amount of ozone as that produced in an oxygen DBD. In addition, humidity in the air reduces the ozone generation performance. It should also be noted that nitrogen oxides are produced in an air DBD. Experiments were carried out with air, dried air and synthetic air (80 % N_2 + 20 % O_2).

The NO_x concentration at the outlet of the scrubber was measured for various settings of the power and air flow rates through the DBD. The mixing temperature was set to 140 °C. The results are shown in figure 5. 70 % NO_x removal required an air flow rate of 35 SLM and a DBD power of 500 W. Tests at higher flow rates and powers were not performed. The DBD ozone generator was not designed to such high flow rates and input powers. For the air DBDs the ratio of the O_3 consumption to the amount of removed NO_x was about 2 which is comparable with that for oxygen DBDs (see figure 3).

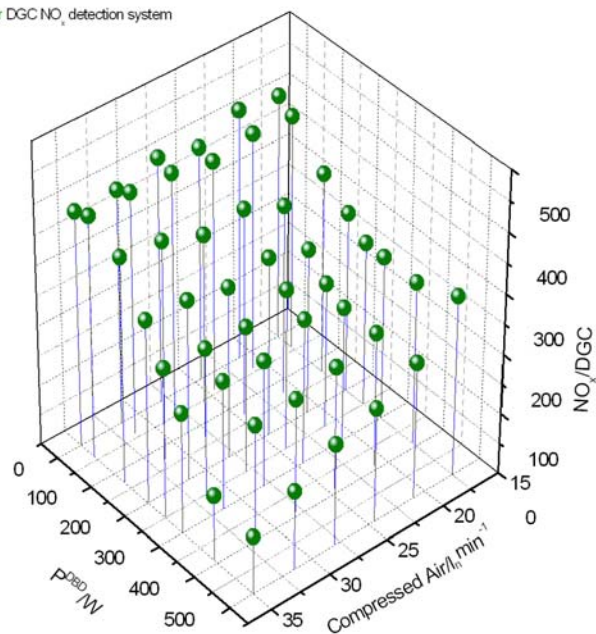


Figure 5. NO_x concentration measured with the chemiluminescence NO_x analyzer at the scrubber outlet for various power settings and air flow rates through the DBD. The mixing temperature was 140 °C.

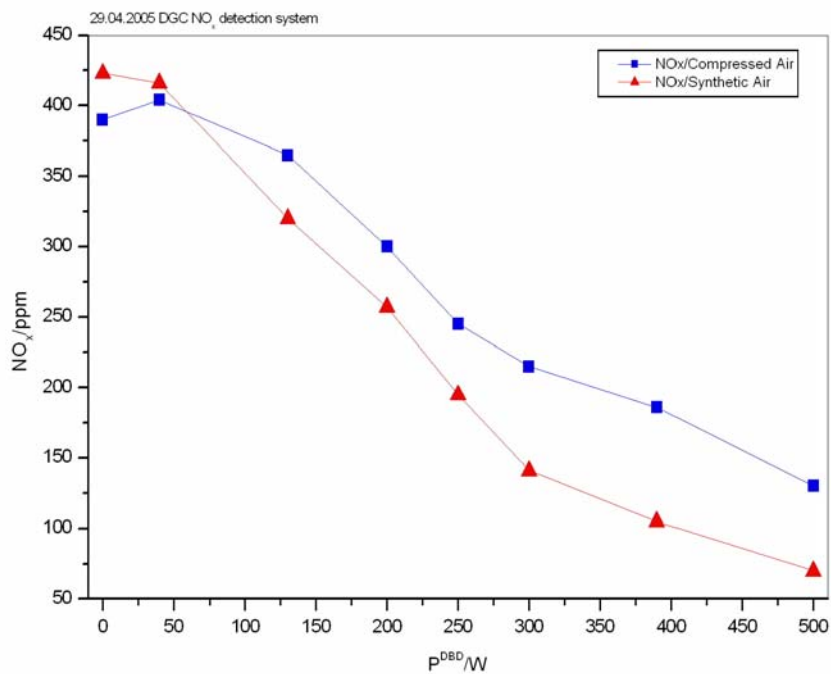


Figure 6. NO_x concentration measured with the chemiluminescence NO_x analyzer at the scrubber outlet for various power settings with different feed gases for the DBD: air (blue); synthetic air (red). The mixing temperature was 140 °C and the flow rate was 31.5 SLM.

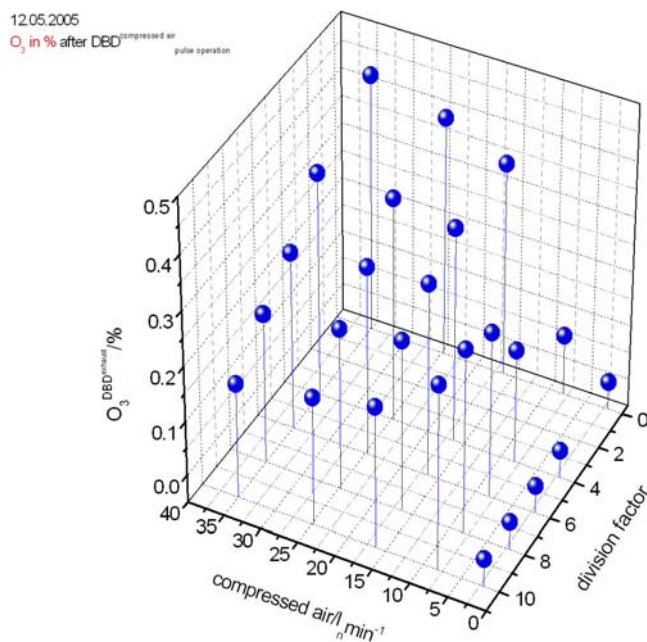


Figure 7. Ozone concentration measured at the DBD outlet at various power settings and flow rates of the dried compressed air. The division factor is the ratio of the operation (pulse) frequency to the pulse repetition frequency (for a division factor N larger than 3 the power is given as $1800 \text{ W}/N$. Division factor “0” corresponds to cw-operation).

The ozone production efficiency in an air DBD can be increased if dry or synthetic air is used as feed gas. Figure 6 shows the NO_x removal efficiency for a compressed air fed DBD gas compared with that for a synthetic air fed DBD. The synthetic air DBD was more efficient than the compressed air DBD. At a power input of 500 W about 90 % NO_x removal was observed with the synthetic air feed DBD. It was also found that the ozone production efficiency could be increased by about 0.1 % when the air used as feed gas for the DBD was dried by guiding it through a chamber filled with silica pallets. The formation of ozone in a DBD driven by dried air for various power settings and air flow rates is shown in Figure 7. It is noted that at low flow rates, high power input can also reduce the ozone formation performance.

IR absorption spectroscopy showed that the N_2O emission measured after the scrubber was of the order of 2 – 5 ppm when compressed air was used as the DBD feed gas.

During the experiments the pH level of the water in the water tank for the scrubber was measured between 1 and 5.

4 Energy consumption

Measurements of the DBD power input showed that the energy required to remove one mol NO_x varies between 0.5 and 2.5 kWh/mol NO_x (18.7 and 93.5 eV/ NO_x molecule) for an oxygen DBD (Figure 8). For an air DBD the energy required to remove one mol NO_x was found to vary between 2 and 4.5 kWh/mol NO_x (74.6 and 167.9 eV/ NO_x molecule). With an O_3 consumption of 1.5 mol per reduced mol NO_x (see section 1) and an O_2 dissociation energy of 5.1 eV, the lower limit of the energy required to remove one mol NO_x can be estimated to 0.1 kWh/mol NO_x (3.8 eV/ NO_x molecule) which indicates that the energy efficiency of the ozone production in the DBD can be improved. The energy consumption has been considered as the energy supplied to the DBD. The energy losses in the electronics of the power supply (incl. the transformer) have not been included. As mentioned previously, 95 % removal was achieved at a temperature of 160 °C, an oxygen flow rate of 6 SLM and a DBD power of 390 W. At a DBD power of 390 W the total power consumption by the power supply was measured to 662 W. Taking into account that only 10 % of the total exhaust was treated, this corresponds to about 22 % of the engine power. At a temperature of 110 °C, 95 % NO_x removal was achieved at a DBD power of 250 W which shows that the energy consumption can be reduced to less than 15 % of the engine power for 95 % NO_x removal. For ozone injection from an air DBD the power consumption for 70 % NO_x removal (140 °C, air flow rate of 35 SLM, DBD power of 500 W) was about 30 % of the engine power. As discussed above, the efficiency of the ozone production from compressed air may be improved by drying the air.

It should be emphasised that the equipment used for demonstration of NO_x removal was not optimized with respect to energy efficiency and costs. For a commercially available ozone generator the energy consumption corresponds to 8 % of the power of the power plant (3 MW) for 95 % NO_x removal with oxygen as the feed gas, or 70 % NO_x removal with air as the feed gas (see Appendix 3, NO_x Emission Control Using Low Temperature Plasma, Economical Evaluation).

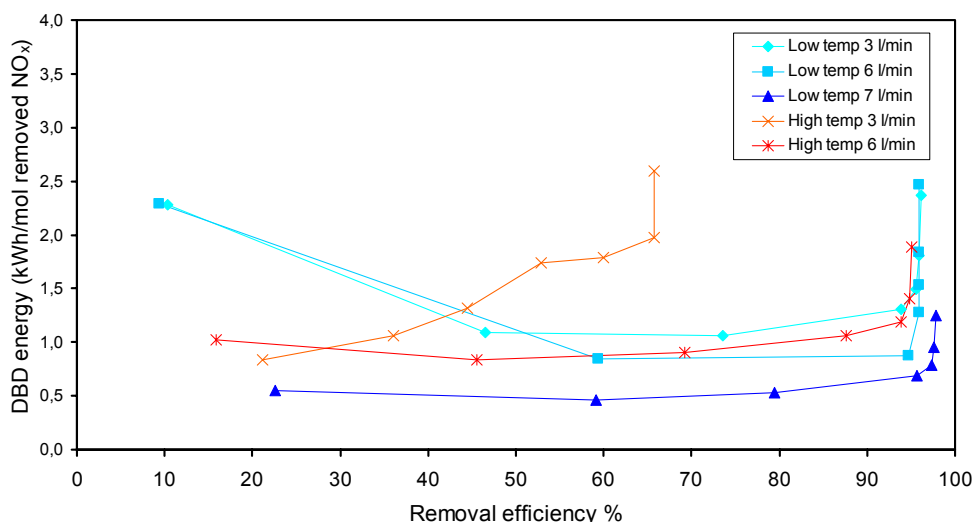


Figure 8. The energy required to remove one mol NO_x versus the removal efficiency for tests performed with an oxygen DBD.

Appendix 3

NO_x Emission Control Using Low-Temperature Plasma

Economic Evaluation

Michael Ørtenblad

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Hørsholm 2005

1. Introduction

The objective of this report is to describe the costs involved in the establishment and operation of a NO_x reduction plant based on reduction by means of ozone. The report is based on information obtained from suppliers of equipment and other suppliers and based on results from tests made during the project.

First, the report describes investment costs. This part also describes costs for the ozone production unit, reactor and absorption system. Next, the operating costs are described, based partly on actual industrial prices and partly on experience from similar processes. This part describes man-time, ozone production, cooling, scrubber and water treatment and depreciation of equipment.

Finally, Annex 1 describes simple tools for optimization of operation parameters for ozone production according to operating costs. Annex 2 shows detailed tables of total operating costs for industrial plants of 1 and 3 MW.

2. Investment costs

Investment costs include every piece of equipment for the NO_x reduction plant. According to the plant description the NO_x reduction plant can be divided into three sections to better illustrate the necessary investments:

- Ozone production unit
- Reactor
- Absorption system

2.1 Ozone production unit

The ozone production unit is one section. This section includes a DBD ozone generator, a power supply and an oxygen supply system.

Calculations based on results from the tests at 110 °C show that approx. 8 kg ozone/hour are needed for a 1 MW plant, and approx. 25 kg ozone/hour are needed for a 3 MW plant. Similarly at 160 °C, approx. 13 kg ozone/hour are needed for a 1 MW plant and approx. 38 kg ozone/hour for a 3 MW plant.

On inquiry, various producers of ozone generators informed us that an ozone generator (with oxygen as ozone medium) of this size can be obtained at a price of DKK 2,580,000 for a 3 MW plant, with NO_x reduction at 110 °C. The price for a similar ozone generator for a 1 MW plant is estimated at approx. DKK 1,200,000. If pressurized air is used as ozone medium, and the NO_x reduction will take place at max. 140 °C, the price for the ozone generator is estimated to be around DKK 2,400,000 for a 1 MW plant and around DKK 4,700,000 for a 3 MW plant. The extra purchase price is due to expenses for a drying system and a compressor for the air.

2.2 Reactor

The second part of the system is the reactor. The function of this section is to provide sufficient residence time for the reaction to occur. The estimated necessary residence is in the order of one second; hence it is on most plants possible to utilise the flue gas duct already in place. Due to this, no cost has been attributed to the reactor.

2.3 Absorption system

The last section is the absorption system, consisting of scrubber and water treatment system. The main purpose is to absorb the N_2O_5 generated and treat the wastewater. The size of the absorption system will vary with the plant size. If there is already a scrubber at the plant, it can be used, and, probably, a separate absorption system will not be necessary.

DGC has knowledge of a similar absorption system, designed for a 1 MW gas engine plant (lean burn), which had a price, including tanks, pumps, piping, etc., of approx. DKK 200,000. It is estimated that upscaling to e.g. a 3 MW plant will incur an increase in price of approx. DKK 50-100,000.

3. Operating costs

Operating costs are divided into four groups: man hours, ozone production (cooling), water treatment and current depreciation on the plant. Detailed tables of operating costs for both 1 and 3 MW plants are given in Annex 2.

3.1 Man hours

It is assumed that daily inspection will take 5 min/day, maintenance 2 hours/ month and annual inspection 10 hours/year + repairs, if any. These assumptions are used as basis for the calculation of the time consumption of daily inspection and general maintenance. With an estimated price per hour of DKK 300 the operating costs will amount to DKK 1.49/kg $\text{NO}_{2,\text{reduced}}$ in the examples used.

3.2 Ozone production

The operating costs for ozone production are made up of power consumption for the plasma generator and oxygen consumption. This part is by far the largest part of the operating costs when oxygen is used as ozone medium. Calculations based on prices obtained for 1 and 3 MW plants, respectively, show that operating costs for ozone production with oxygen as ozone medium and NO_x reduction at 110 °C amount to approx. DKK 20/kg $\text{NO}_{2,\text{reduced}}$ and, correspondingly, to approx. DKK 25/kg $\text{NO}_{2,\text{reduced}}$ for reduction at 160 °C. If pressurized air is used as ozone medium instead, the costs for ozone production are as low as approx. DKK 7.5/kg $\text{NO}_{2,\text{reduced}}$.

At e.g. 95 % NO_x reduction, the figures in Annex 1 show that operating costs during the tests of ozone production with oxygen as ozone medium amounted to DKK 32,47/kg $\text{NO}_{2,\text{reduced}}$ at 110 °C and DKK 42,59/kg $\text{NO}_{2,\text{reduced}}$ at 160 °C. It is estimated that the cost reduction potential will be up to 70-80 % for the equipment used.

3.3 Cooling

The flue gas is cooled prior to reaching the reactor. The costs depend on the cooling need. Most stationary processes utilize the heat produced. Therefore, it is not necessary to cool the flue gas. Cooling may be necessary at mobile plants, like ships, cars, trains etc., as these plants typically do not utilize the heat produced.

3.4 Scrubber and water treatment

The water treatment section only accounts for a small part of the total operating costs. Circulation of water and supply of make-up water only amounts to between DKK 0.26 and DKK 0.53/kg $\text{NO}_{2,\text{reduced}}$ in the examples used.

Before the process water is discharged, it needs to be acid-base neutralized. The cheapest method is to add Calcium Carbonate (CaCO_3). Alternatively, Sodium Hydroxide (NaOH) can be used, but this method would considerably increase the operating costs. The operating costs for the finishing of the process water and the discharge amount to between DKK 0.15 and 0.33/kg $\text{NO}_{2,\text{reduced}}$. The utilisation of the nitrate wastewater as a fertilizer could be beneficial, but the subject has not been evaluated in this project.

3.5 Depreciation on equipment

The NO_x reduction plant is depreciated through the operating costs. The examples used in this report calculate with a payback time of 15 years and an interest rate of 6 %. Costs in connection with depreciation depend on the size and efficiency of the plant. The examples used with oxygen as ozone medium have depreciation costs between DKK 6 and 10/kg $\text{NO}_{2,\text{reduced}}$. The depreciation on ozone plants using pressurized air as ozone medium is much higher than on the plants using oxygen as ozone medium. The reason being larger plant investments. The depreciation on these plants makes out the greater part of the operating costs for plants with pressurized air as ozone medium.

3.6 Total operating costs

The total operating costs calculated for the examples used can be seen in Table 1.

Table 1. Calculated total operating costs for NO_x reduction with ozone

Plant size	MW	1	3	1	3	1	3
Operation temperature	°C	110	110	160	160	140	140
Ozone medium		Oxygen	Oxygen	Oxygen	Oxygen	Air	Air
Total operating costs	DKK/kg $\text{NO}_{2,\text{reduced}}$	32.33	27.24	36.43	31.33	30.56	20.93

4. Conclusion

The total cost of the NO_x reduction method using ozone has been estimated according to the NO_x levels and ozone consumption observed in the laboratory scale experiments. The total cost of NO_x reduction varies between DKK 20 and 35 per kg NO_x reduced.

The major part of the NO_x reduction cost is attributed to the ozone generation as operating or investment costs. The specific NO_x reduction cost is estimated to be lower the larger the plant and the cooler the exhaust gas temperature.

Use of air for ozone generation seems favourable compared to oxygen. The difference in total cost is due to a large reduction in operating cost (oxygen cost) and an increased investment (air treatment).

The investment and operating cost for ozone generation is based on commercial equipment for ozone generation. The equipment is normally used in industries and processes where high ozone concentrations are needed. There might be a potential for further cost reductions in optimising the ozone generating process towards flue gas cleaning, where high ozone concentrations might not be needed.

Annex 1

The ozone production was continuously observed during tests. The tests were performed with variable effect on the ozone generator (DBD effect) and variable oxygen flow through the generator.

The DBD effect was stepwise variable from 0-500 W resulting in increasing ozone formation. Similarly, the oxygen flow was stepwise variable from 1.4-6 normal litres per minute. Variation of these two parameters results in varied ozone formation and thus various levels of NO_x reduction. The NO_x reduction related to the costs of the different settings of the two parameters makes it possible to find an operation optimum for a given operation situation within the tested parameter range.

Table 2 is based on three different test series.

Table 2. Parameters from selected test series

Series	Date	Effect	Oxygen flow	Temperature	Ozone medium
		W	l _n /min	°C	
#1	28-04-2005	0 - 500	1,4 - 6	160	Pure O ₂
#2	04-05-2005			110	Pure O ₂
#3	29-04-2005			140	Pressurized air (dry)

The test results show that the DBD effect, the temperature as well as the ozone medium greatly affect the level of NO_x reduction. Comparing the results with the calculated operating costs for the tests demonstrates the operating costs for ozone formation in relation to the level of reduction at the given temperatures for any operation situation within the tested parameter range.

Figures 1 to 3

The below figures show the NO_x reduction level as a function of the DBD effect and the oxygen/pressurized air flow during tests. Figure 1 and Figure 2 illustrate that it is easier to achieve higher reduction levels at a process temperature of 110 °C than at a temperature of 160 °C. Both tests used pure oxygen as ozone medium.

From Figure 1 it appears that more than 5 normal litres oxygen/min. and min. 400 W in the DBD unit at a flue gas temperature of 160 °C are necessary to achieve reduction levels at approx. 95 %. Increases in both parameters will only increase the reduction level marginally. Figure 2 shows that reduction levels of around 95 % at a flue gas temperature of 110 °C can be achieved already at an oxygen flow of 3 normal litres oxygen/min. and a DBD effect of 250 W. It is, obviously, easier to reach high reduction levels at that temperature than at 160 °C, which - on the other hand - results in lower operating costs.

Figure 3 shows that dry pressurized air (oxygen content approx. 21 %) results in lower reduction levels. This is due to the fact that the lower oxygen content results in a smaller amount of ozone, which - in turn - results in less conversion of NO_x. The figure shows that under the given circumstances reduction levels of approx. 75 % can be achieved.

28042005, $T_3 = 160\text{ C}$, O_2

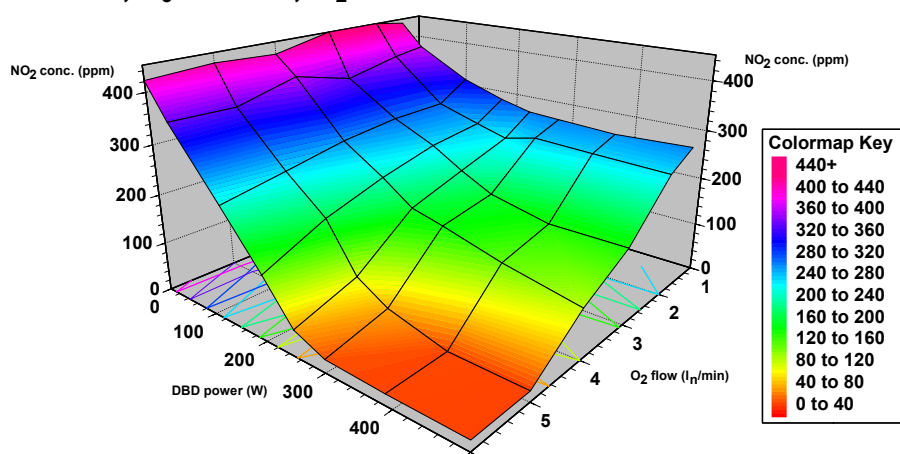


Figure 1. NO_x reduction as a function of DBD effect and oxygen flow at 160 °C and with pure O_2 as ozone medium.

04052005, $T_3 = 110\text{ C}$, O_2

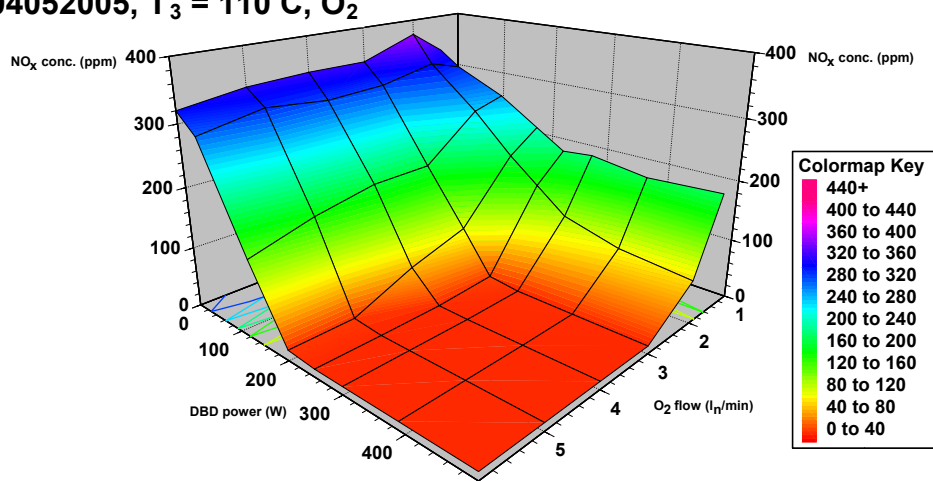


Figure 2. NO_x reduction as a function of DBD effect and oxygen flow at 110 °C and with pure O_2 as ozone medium.

29042005, $T_3 = 140\text{ °C}$, Air

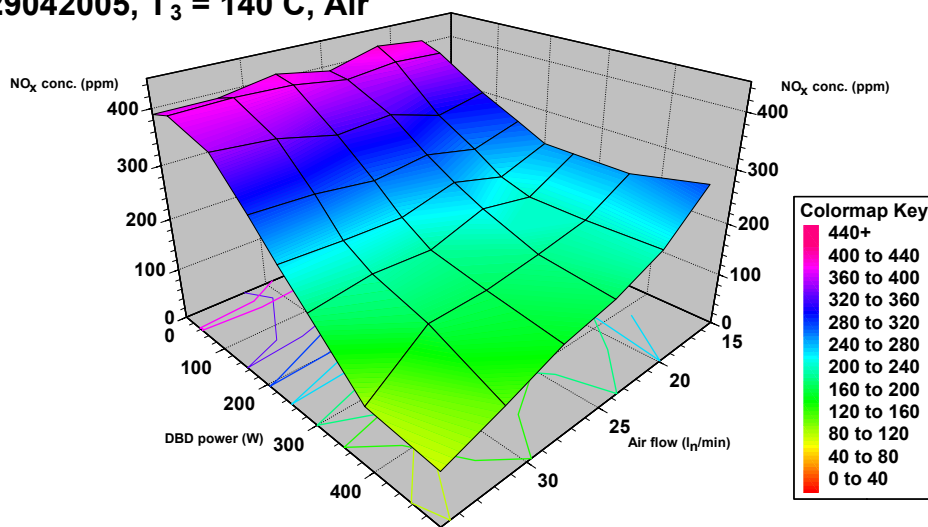


Figure 3. NO_x reduction as a function of DBD effect and oxygen flow at 140 °C and with pressurized air as ozone medium.

Figures 4 to 6

The below figures show the total operating costs for ozone production per kg reduced NO₂ as a function of oxygen/pressurized air flow and the DBD effect. The price used for the DBD effect has been multiplied by a factor of two in order to include any effect loss in the equipment.

Figure 4 shows that the total costs for ozone generation per kg reduced NO₂ at 160 °C decreases proportionally with increasing DBD effect. At low effect, hardly no ozone is generated that can reduce NO_x. The figure also shows that at DBD effect above 250 W the costs per kg reduced NO_x hardly decrease. The lowest costs per kg reduced NO₂ are in the range of DKK 40-50/kg reduced NO₂.

Figure 5 (test at 110 °C) shows the same tendency as Figure 4. The only difference, however, is that the lowest operating costs are a bit lower, approx. DKK 30-40 per kg reduced NO₂.

Figure 6 (test at 140 °C with pressurized air) shows that it is cheaper to use pressurized air for ozone generation than it is to use pure oxygen. This is due to the price per m³, which in these calculations has been estimated at DKK 1.20/m³n for oxygen and DKK 0.03/m³n for pressurized air. The graph has a similar course as those for oxygen, and the lowest costs are in the range DKK 20-30/kg reduced NO₂.

28042005, $T_3 = 160\text{ C}$, O_2

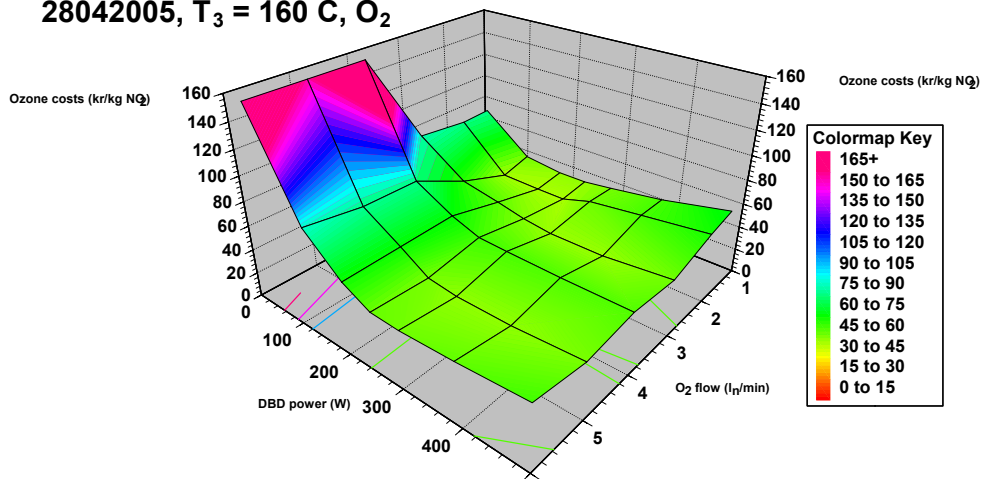


Figure 4. Total operating costs for ozone generation as a function of DBD effect and oxygen flow at 160 °C and with pure O_2 .

04052005, $T_3 = 110\text{ C}$, O_2

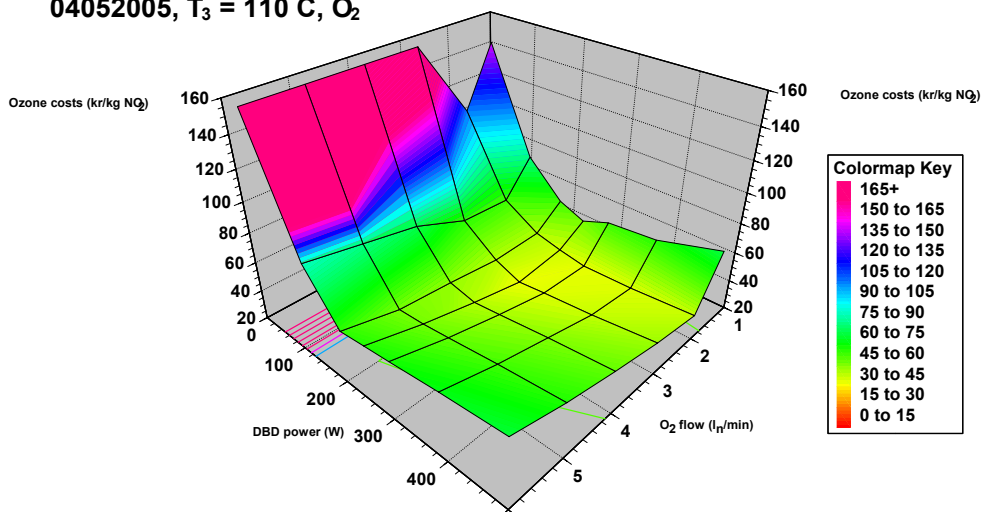


Figure 5. Total operating costs for ozone generation as a function of DBD effect and oxygen flow at 110 °C and with pure O_2 .

29042005, $T_3 = 140\text{ °C}$, Air

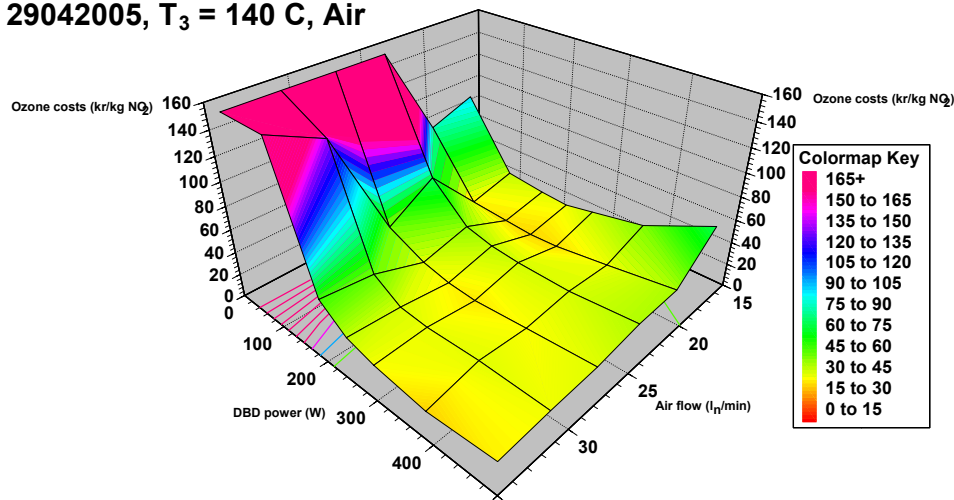


Figure 6. Total operating costs for ozone generation as a function of DBD effect and pressurized air flow at 140 °C and with pressurized air.

Figures 7 to 9

Figure 7 to Figure 9 show reduction costs per kg reduced NO₂ as a function of reduction level for three selected test series at a given temperature and a given ozone medium. The figures may be used for identification of the necessary amount of oxygen/pressurized air to achieve a given level of reduction and at the same time to establish the corresponding costs. The curve representing the lowest reduction costs at a given level of reduction identifies the given process parameters for oxygen flow per kg NO_{2, in} and DBD effect to be read in the basic data of the figures. This is an efficient tool partly for minimizing the operating costs at a certain reduction level, temperature and ozone medium, and partly for easy identification of parameter settings at the lowest operating costs.

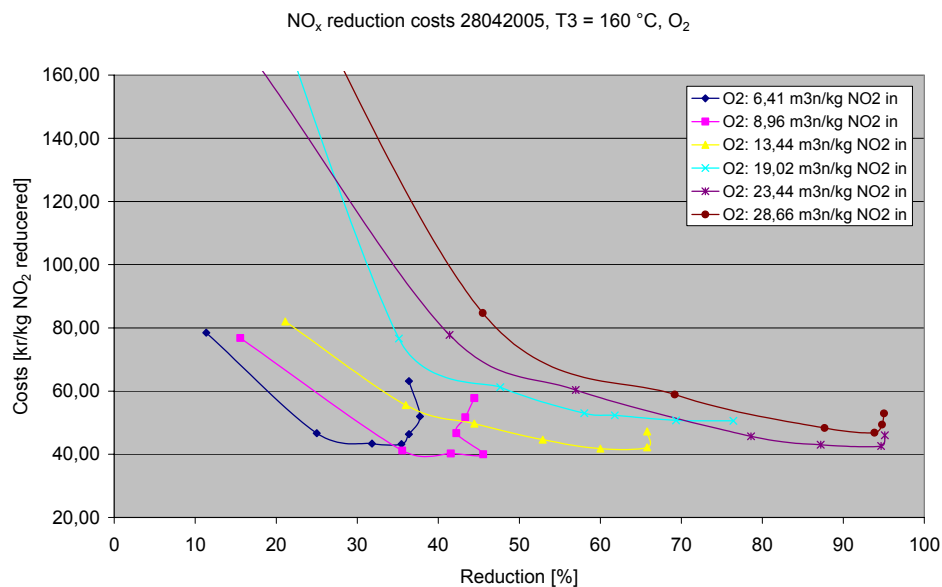


Figure 7. Operating costs at ozone generation as a function of reduction level at 160 °C and with O₂.

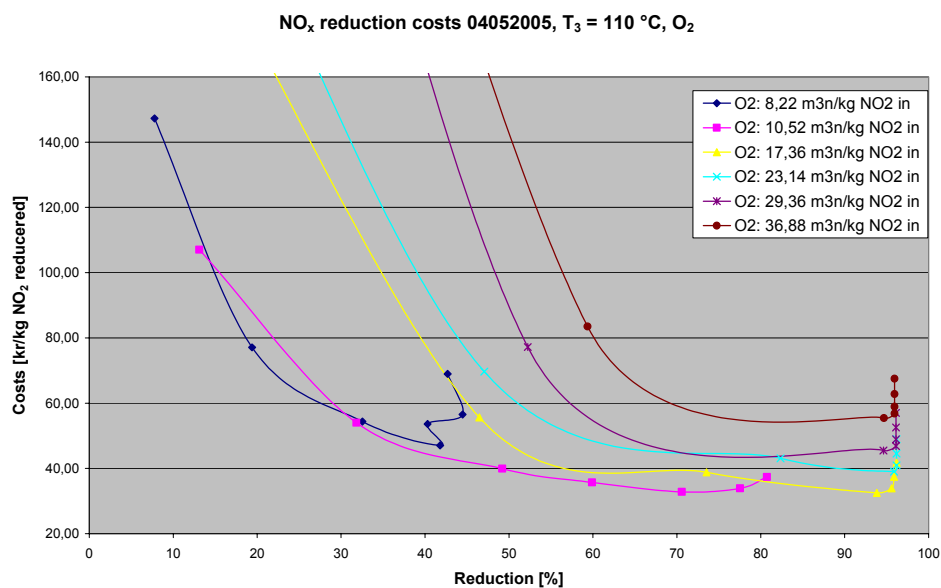


Figure 8. Operating costs at ozone generation as a function of reduction level at 110 °C and with O₂.

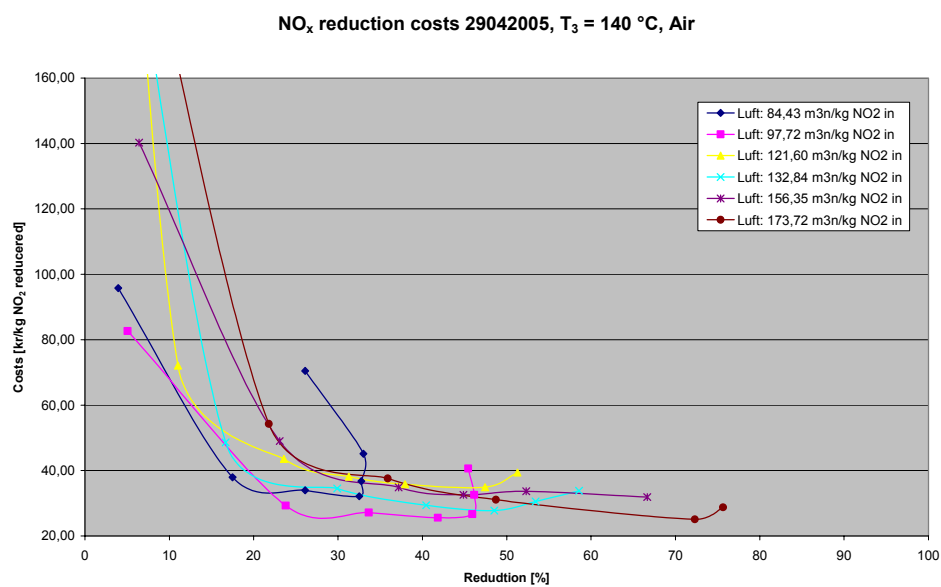


Figure 9. Operating costs at ozone generation as a function of reduction level at 140 °C and with pressurized air.

Risø-I-2380/EN)

Operating Costs, 95% NO_x reduction, Oxygen as ozone medium

Plant size temperature 3.27 °C 10,464 kg/hour 4500 h/year Operating hours engineering hours daily inspection monthly maintenance early inspection early time consumption total working hours estimated pay 300 DKK/hour Operating costs costs per kg NO ₂ reduced Ozone production RED power consumption oxygen consumption (1,20 DKK/m ³ O ₂) Costs calculated from experiments Waste water treatment circulation of water - power used in pumps (5 kW) Make-up water Operating costs costs per kg NO ₂ reduced CaCO ₃ NaOH handling not included special tax for nitrate-rich waste water Operating costs costs per kg NO ₂ reduced Depreciation and interest of equipment price for new absorption unit price for new ozone generation unit Depreciation in 15 years rate of interest is set at 6% annual payment Operating costs costs per kg NO ₂ reduced total operating costs for NO _x reduction	1 MW 110 °C 3.27 kg/hour 4500 h/year h/day h/month h/year 10 24 64.42 19325 DKK 4.29 DKK/hour 1.31 DKK/kg NO ₂ 0.20 DKK/kW (64 kW) (45 m ³ O ₂ /h) 3.91 DKK 16.51 DKK 20.43 DKK/kg NO ₂ 0.20 DKK/kW (0.06 m ³ /h) (100 kg NaNO ₂ /m ³ water) 1.60 DKK/hour 0.49 DKK/kg NO ₂ 3.55 kg/h - 100 DKK/ton 2.84 kg/h - 6,10 DKK/kg 0.65 DKK 1.00 DKK/hour 0.31 DKK/kg NO ₂ 200,000 DKK 1,200,000 DKK 1,400,000 DKK 144,147.87 DKK 32.03 DKK/hour 9.80 DKK/kg NO ₂ 32.33 DKK/kg NO ₂	3 MW 110 °C 10,464 kg/hour 4500 h/year h/day h/month h/year 10 24 64.42 19325 DKK 4.29 DKK/hour 0.41 DKK/kg NO ₂ 0.20 DKK/kW (240 kW) (135 m ³ O ₂ /h) 4.59 DKK 15.48 DKK 20.07 DKK/kg NO ₂ 0.20 DKK/kW (0.2 m ³ /h) (100 kg NaNO ₂ /m ³ water) 3.00 DKK/hour 0.29 DKK/kg NO ₂ 11,37 kg/h - 100 DKK/ton 9.1 kg/h - 6,10 DKK/kg 0.67 DKK 1.81 DKK/hour 0.17 DKK/kg NO ₂ 300,000 DKK 2,580,000 DKK 2,880,000 DKK 296,532.76 DKK 65.90 DKK/hour 6.30 DKK/kg NO ₂ 27.24 DKK/kg NO ₂	1 MW 160 °C 4.17 kg/hour 4500 h/year h/day h/month h/year 10 24 64.42 19325 DKK 4.29 DKK/hour 1.03 DKK/kg NO ₂ 0.20 DKK/kW (104 kW) (71 m ³ O ₂ /h) 4.99 DKK 20.43 DKK 25.42 DKK/kg NO ₂ 0.20 DKK/kW (0.077 m ³ /h) (100 kg NaNO ₂ /m ³ water) 1.77 DKK/hour 0.42 DKK/kg NO ₂ 4.53 kg/h - 100 DKK/ton 3.63 kg/h - 6,10 DKK/kg 0.51 DKK 0.96 DKK/hour 0.23 DKK/kg NO ₂ 200,000 DKK 1,500,000 DKK 1,700,000 DKK 175,036.70 DKK 38.90 DKK/hour 9.33 DKK/kg NO ₂ 36.43 DKK/kg NO ₂	3 MW 160 °C 13,344 kg/hour 4500 h/year h/day h/month h/year 10 24 64.42 19325 DKK 4.29 DKK/hour 0.32 DKK/kg NO ₂ 0.20 DKK/kW (365 kW) (207 m ³ O ₂ /h) 5.47 DKK 18.62 DKK 24.09 DKK/kg NO ₂ 0.247 m ³ /h (100 kg NaNO ₂ /m ³ water) 3.47 DKK/hour 0.26 DKK/kg NO ₂ 14.50 kg/h - 100 DKK/ton 11.60 kg/h - 6,10 DKK/kg 0.53 DKK 1.98 DKK/hour 0.15 DKK/kg NO ₂ 300,000 DKK 3,500,000 DKK 3,800,000 DKK 391,258.50 DKK 86.95 DKK/hour 6.52 DKK/kg NO ₂ 31.33 DKK/kg NO ₂
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Operating Costs, 70% NO_x reduction, Air as ozone medium

Plant size	1 MW			3 MW		
	140 °C	2.89 kg/hour	4500 h/year	140 °C	9.25 kg/hour	4500 h/year
Temperature						
NO_x reduction						
Operating hours						
Engineering hours						
Daily inspection	h/day	0,083	h/month	h/day	0,083	h/month
Monthly maintenance		2,00			2,00	
Yearly inspection		10			10	
Yearly time consumption		30,42	24		30,42	24
Total working hours		64,42			64,42	10
Estimated pay 300 DKK/hour			19325 DKK			19325 DKK
Operating costs			4,29 DKK/hour			4,29 DKK/hour
Costs per kg NO ₂ reduced			1,49 DKK/kg NO₂			0,46 DKK/kg NO₂
Ozone production						
DED power consumption	0,20 DKK/kW (75 kW)	5,19 DKK		0,20 DKK/kW (240 kW)	5,19 DKK	
Oxygen consumption	(0,03 DKK/m ³ Air)	(235 m ³ lufth)	2,44 DKK	(750 m ³ lufth)	2,43 DKK	
Costs calculated from experiments			7,63 DKK/kg NO₂			7,62 DKK/kg NO₂
Waste water treatment						
Circulation of water - power used in pumps (5 kW)						
Make-up water	0,20 DKK/kW	1,00 DKK		0,20 DKK/kW	1,00 DKK	
Operating costs	(0,053 m ³ /h)	0,63 DKK		(0,171 m ³ /h)	1,71 DKK	
Costs per kg NO ₂ reduced	(100 kg NaNO ₂ /m ³ water)	1,53 DKK/hour	0,53 DKK/kg NO₂	(100 kg NaNO ₂ /m ³ water)	2,71 DKK/hour	0,29 DKK/kg NO₂
CaCO ₃						
(NaOH)	3,14 kg/h - 100 DKK/ton	0,31 DKK		10,05 kg/h - 100 DKK/ton	1,01 DKK	
Handling not included	2,51 kg/h - 6,10 DKK/kg	15,31 DKK		8,04 kg/h - 6,10 DKK/kg	49,04 DKK	
Special tax for nitrate-rich waste water						
Operating costs		0,65 DKK			0,65 DKK	
Costs per kg NO ₂ reduced		0,96 DKK/hour	0,33 DKK/kg NO₂		1,66 DKK/hour	0,18 DKK/kg NO₂
Depreciation and interest of equipment						
Price for new absorption unit						
Price for new ozone generation unit	200.000 DKK			300.000 DKK		
Depreciation in 15 years	Estimate!	2.400.000 DKK		4.700.000 DKK		
Rate of interest is set at 6%		2.600.000 DKK		5.000.000 DKK		
Annual payment						
Depreciation in 15 years						
Rate of interest is set at 6%						
Annual payment		267703,19 DKK		514813,82 DKK		
Operating costs			59,49 DKK/hour			114,40 DKK/hour
Costs per kg NO ₂ reduced			20,58 DKK/kg NO₂			12,37 DKK/kg NO₂
Total operation costs for NO_x reduction			30,56 DKK/kg NO₂			20,33 DKK/kg NO₂

Risø's mission

- to create new knowledge based on world-class research, and
- to ensure that our knowledge is used to promote the development of an innovative and sustainable society

Risø's vision

In close dialogue with the business sector, the political system and the research community, we create new

- opportunities for the energy systems of the future
- technological possibilities for diagnosis and treatment of diseases
- knowledge-based products and business enterprises with growth potential